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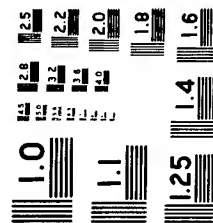
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(STUDIES IN THE CORROSION OF ALUMINIUM BASE
ALLOYS IN WATER AT VARIOUS pH VALUES)

PART I

"Corrosion of aluminium base nickel, silicon & magnesium alloys"

by

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ABSTRACT

The influence of pH on the corrosion of aluminium base nickel, silicon alloy with and without magnesium in water of pH 5, 6.5 and 8 at 30°, 85° and 100°C has been studied by weight loss and electrochemical methods. The Al-9% Si-1% Ni alloy has better corrosion resistance than Al-9% Si-1% Ni-1% Mg alloy at the pH values and the temperatures reported. The corrosion rate is found to be maximum at pH 8 at these temperatures for both the alloys. The results obtained have been compared with corrosion behaviour of aluminium 1S in water at various pH values and temperatures.

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STUDIES IN THE CORROSION OF ALUMINUM BASE
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PART I. "Corrosion of aluminum base nickel, silicon & magnesium alloys".

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INTRODUCTION

Aluminum finds extensive application as fuel element, cladding material in water-cooled reactors due to its cheapness and ease of fabrication or as a material of low neutron absorption cross section. Several aluminum base alloys⁽¹⁾ have been developed with adequate mechanical strength at elevated temperatures and corrosion resistance in water at high temperature. However, the low creep strength of these wrought alloys tend to limit their use at high temperatures of 250° to 300°C. Sintered aluminum products⁽²⁾ or dispersion-hardened aluminum with alumina⁽³⁾ and aluminum base alloys containing silicon, nickel and magnesium⁽⁴⁾ are of current interest for use as cladding material. Information on the corrosion resistance of Al-9% Si-1% Ni and Al-9% Si-1% Ni-1% Mg alloys in water below 100°C has been lacking. It is known⁽⁵⁾ that the corrosion of aluminum alloys in water at low temperatures is rapid at the beginning of the exposure and thereafter diminishes. In the range 30° to 100°C the corrosion rates are low in pure water and are of academic interest. However, pH of water has considerable influence even at these temperatures. Measurable corrosion rates may be observed at temperatures below 100°C by varying the pH of the water. The present work is devoted to the weight loss and variation of potential with time of Al-9% Si-1% Ni and Al-9% Si-1% Ni-1% Mg alloys in water of pH 5, 6.5 and 8 at 30°, 65° and 100°C. The anodic and cathodic polarisation measurements (potentiostatically) in water of pH 5, 6.5 and 8 at 30°C have been made. The results obtained are compared with those of aluminum-18 under similar conditions.

EXPERIMENTAL

The Al-9% Si-1% Ni and Al-9% Si-1% Ni-1% Mg alloy specimens prepared from

* The composition indicated is the nominal composition

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extruded tubes and Al-1S specimens were polished with successive grades of emery paper. They were degreased in benzene and acetone, dried, weighed and their surface areas measured accurately. They were immersed in water of various values of pH for weight loss measurements (H_2SO_4 and $LiOH$ being used to adjust the pH at 30°C). The electrode potential-time measurements have been carried out with Cambridge Vernier potentiometer using mercury-mercurous sulphate, saturated potassium sulphate electrode as the reference ($Hg/Hg_2SO_4/Sat.K_2SO_4$) and the values have been converted to saturated calomel electrode values for convenience. The anodic and cathodic polarisation studies in these solutions have been carried out using a Wenking potentiostat with platinum as the auxiliary electrode.

The specimens on removal from the solution after immersion test, have been washed well in running water, degreased in acetone, dried and weighed. The weight loss in milligrams has been converted to milligrams per square decimetre per day (mdd) on the basis of definite time in days of immersion test. Al-1S specimens after corrosion, have been treated in 4 g. CrO_3 + 10 ml. H_3PO_4 in 100 ml. water at 85°C, until free of corrosion products and the weight loss determined after deducting the blank correction.

RESULTS AND DISCUSSION

From Table I, in the case of Al-9% Si-1% Mg alloy with temperature rise in the range 30° to 100°C the influence of pH on the corrosion rate is observed in a steep initial rise upto 85°C and then a gradual change upto 100° at pH 5; a gradual fall at pH 6.5 with rise in temperature and a sharp rise at 85°C from a low value at 30°C and then a fall to a value almost corresponding to the value at pH 8. The maximum corrosion rate occurs at pH 8 at a temperature of 85°C the value being 15.92 m.d.d. There is no perceptible corrosion at pH 5 at a temperature of 30°C.

In the case of Al-9% Si-1% Mg alloy with rise in temperature in the range 30° to 100°C, the influence of pH on the corrosion rate is seen as a slight rise up to temperature of 85°C and then a slight decrease at pH 5. At pH 6.5 the initial high rate of weight gain at 30°C decreases to a low value of loss in weight at 85°C, the corrosion rate rising again at 100°C and observed as a weight gain. At pH 8 there is a continuous rise in corrosion rate with temperature the maximum value being observed as 56.40 m.d.d. at 100°C. As in the case of Al-9% Si-1% Mg alloy there is no corrosion in water of pH 5 at 30°C.

Comparing the useful range of application of the two alloys Al-9% Si-1% Mg & Al-9% Si-1% Mg, it can be seen that it is advantageous to use Al-9% Si-1% Mg alloy at

pH 5, the corrosion rate being lower compared to the former at all temperatures. At pH 6.5 both the alloys behave almost in an identical fashion. At pH 8 Al-9% Si-1% Mg alloy is decidedly superior in its corrosion behaviour to the latter alloy at all temperatures.

At all the three temperatures studied while the electrode potentials tend to be anodic with time at pH 5, the tendency is towards being cathodic (noble) in the case of both the alloys at pH 8. At pH 6.5, in the case of Al 9% Si-1% Mg while the variation of potentials with time is not influenced at 85° & 100°C, there is a tendency to be anodic at 30°C. Similar anodic tendency is exhibited by Al-9% Si-1% Mg alloy at 85°C while variation of potentials with time is not marked at 30°C & 100°C.

From Table 2 it is observed that the corrosion process control is almost mixed at pH 5, cathodic at pH 6.5 & anodic at pH 8 in the case of Al-9% Si-1% Mg alloy. The control is all anodic for the alloy containing magnesium in addition.

Weight loss and electrode potential-time measurements were carried out in the case of Al-1S under similar conditions for comparison. It is observed from Table 3 that with rise in temperature from 30° to 100°C while influence of pH is not perceptible at pH 6.5, at pH 8, there is a sharp rise with increase in temperature. At pH 5 though the corrosion rate increases upto 85°C, there is a decrease in rate at 100°C. Similar behaviour is observed in the case of Al-9% Si-1% Mg alloy.

The electrode potentials have a tendency to be anodic with time at 85°C and noble at 30°C at all the values of pH studied. However the tendency is variable at 100°C.

The corrosion process is under anodic control at pH 6.5 & 8 the behaviour at pH 8 being similar to that of the other alloys. At pH 5 the control is almost mixed, similar to the behaviour of Al 9% Si-1% Mg alloys. At pH 6.5 particularly the corrosion control changes from anodic at 30°C to cathodic at 40°C.

The corrosion rates of Al-1S are generally higher than those of the alloys except at temperatures of 85° & 100°C at pH 8 where they are slightly lower but are of the same order as the other alloys.

Dreley and Ruther⁽⁶⁾

studied the corrosion of type 1100 aluminium in aerated water at various pH values with various velocities (flow) of water at room temperature. From the results presented in Table 4, the corrosion of Al 1S in water at various values of pH, the effect of temperatures on the corrosion rate in water of pH 8 and 12 has been calculated. It is found that the activation energy values for the corrosion process is of

the order of 4.24 and 3.43 K.cals/mole in the temperature range 28° to 90°C and 65° to 100°C for pH 2 and 12 respectively. The corrosion rate is nine times at pH 12 than at pH 2 at 28°C, the corrosion rate being higher than that at 65°C in pH 12 (Table 4). Dralcy and Ruther⁽⁶⁾ have observed in their paper on the corrosion of type 1100 aluminium alloy at low temperatures in distilled water of pH 5 and 8 that the corrosion rates are small and weighing errors for samples which must be corroded cast doubts on the determination of the slopes from the rate of corrosion versus time curve. However, they have determined the activation energy value at temperatures above 100°C upto 260°C and it has been found to be about 16 K.cals/mole. They are of the opinion that much lower activation energy values may be expected at temperatures lower than 100°C. These different activation energy values below and above 100°C may indicate that the corrosion product below 100°C is likely to be β - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ while that above 100°C may be γ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. In the present work, low activation energy values of 4.24 and 3.43 K.cals/mole in water at pH 2 and 12 show that the corrosion products may be of β - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ type. This mechanism may be in general true for the Al-9% Si-1% Mn and Al-9% Si-1% Mn-1% Mg alloys considering the data obtained by Dralcy and Ruther⁽⁶⁾. The nature of the attack at lower temperatures is that while aluminium is corroding it repairs breaks and faults in its protective oxide film. Videm⁽⁷⁾ is of the view that at room temperature protective films on aluminium are formed in non-complexing solution in the pH range 4 to 8.5.

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TABLE I

WEIGHT LOSS AND ELECTRODE POTENTIAL TIME MEASUREMENTS OF
ALUMINIUM BASE, SILICON, NICKEL AND MAGNESIUM ALLOYS IN
WATER AT VARIOUS TEMPERATURES AND pH VALUES

Type of alloy	pH of water	Temperature	Potential in mv vs S.C.E. upto 4 days from open circuit potential	Corrosion rate based on 4 days immersion test i.e. weight change (mud)	Observation
Al9%Si-1%Ni	5 6.5 8	30°C	-420 -800 -1498	Nil 1.36* 0.91	The Colour of the oxide film after corrosion is dull white grey at pH6.5 and grayish at pH5 and 8.
Al9%Si-1%Ni-1%Ag	5 6.5 8	30°C	-548 -770 -1345	Nil 2.81* 7.57	"
Al9%Si-1%Ni	5 6.5 8	85°C	-480 -950 -1400	3.09 0.82 15.92	"
Al9%Si-1%Ni-1%Ag	5 6.5 8	85°C	-648 -1101 -1513	0.59 0.355 32.80	"
Al9%Si-1%Ni	5 6.5 8	100°C	-540 -790 -1180	3.57* 0.37 1.55	"
Al9%Si-1%Ni-1%Ag	5 6.5 8	100°C	-590 -710 -1200	0.38* 1.53* 56.40	"

* Weight gain

POTENTIOSTATIC POLARISATION MEASUREMENTS OF ALUMINIUM BASE, SILICON, NICKEL AND MAGNESIUM ALLOYS AND Al-1S IN WATER AT 30°C AND AT VARIOUS pH VALUES

TABLE 2

Type of alloy	pH of water	Anodic Polarisation				Current ² in $\mu\text{A}/\text{cm}^2$ observed upto	Cathodic polarisation		Corrosion process
		Potential in mV VS S.C.E.		Current ² in $\mu\text{A}/\text{cm}^2$ observed upto	Potential in mV VS S.C.E.				
		from open circuit potential	To						
Al9%Si-1%Ni	5	-400	+1200	16.97	33.94	-400	-1600	Almost mixed	
	6.5	-500	+1200	1.5×10^3	0.1×10^3	-500	-1800	Cathodic	
	8	-1000	+1800	25.70	25.70	-1000	-1600	Anodic	
Al9%Si-1%Ni-1%Ag	5	-340	+2000	29	6.76	-340	-2000	Cathodic	
	6.5	-470	+2000	8.45	6.8×10^3	-470	-2000	Anodic	
	8	-920	+2000	8.45	2.6×10^3	-920	-2000	Anodic	
Al 18	5	-450	+900	1.15	1-08	-450	-1600	Almost mixed	
	6.5	-350	+800	0.36	289.2	-350	-2000	Anodic	
	8	-1400	+400	0.36	11.44	-1400	-2000	Anodic	
Al 18 at 40°C	5	-475	+800	66.69	47.46	-475	-1700	Almost mixed	
	6.5	-400	+1100	13.33	7.03	-400	-1800	Cathodic	
	8	-1600	+1200	200	207.2	-1600	-2000	Anodic	

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TABLE 3

WEIGHT LOSS AND ELECTRODE POTENTIAL TIME MEASUREMENTS
OF AL-15 AT VARIOUS TEMPERATURES AND pH VALUES

pH of Water	Temperature	Potential in mV vs. S.C.E. upto 4 days		Corrosion rate based on 4 days immersion test i.e. weight change (MDD)	Observation
		From open circuit potential	To		
5	30°C	-820	-620	0.80	The colour of the oxide film after corrosion is dull light grey at pH 6.5 and greyish at other pH values
6.5		-600	-510	2.32	
8		-1010	-410	12.62	
5		-569	-889	16.01	
6.5	85°C	-564	-759	4.92	
8		-714	-1080	16.07	
5		-440	-500	3.42	"
6.5	100°C	-840	-460	3.07	
8	(B.P)	-1250	-1210	30.00	

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TABLE 4

EFFECT OF TEMPERATURE ON THE RATE OF CORROSION OF AL-15

AT pH 2 AND 12

pH of water	Temperature	Corrosion rate based on 4 days immersion test i.e. weight change (M.D.D.)		Activation energy in K.cal/mole.
2	100°C (B.P)		427.1	4.24 between 28°C and 90°C
	90°C		156.4	
	77°C		152.7	
	52°C		103.6	
	28°C		21.73	
12	100°C (B.P)		256.1	3.43 between 65°C and 100°C
	87°C		182.5	
	65°C		127.0	
	28°C		190.3	

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